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STRENGTH ALUMINUM ALLOYS

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An extensive series of experiments have been performed on a 7075 aluminum alloy and its high purity analogue, Al5Zn2.5Mg, in aqueous environments, to determine the role of cathodically evolved hydrogen on fatigue crack initiation and early propagation. Variables in the program include the effects of applied potential, hydrogen damage reversibility, solution pH and mechanical loading modes. Results obtained in the program refute the concept that anionic species need be specific to cause enhanced susceptibility to fatigue cracking, but that hydrogen, both in the presence or absence of significant corrosion, is indeed a potent species for the degradation of fatigue properties. Evidence will be presented that hydrogen, presumed to be associated with the plastic zone at crack tips causes increased crack propagation rates and also results in significant changes in fracture surface morphologies. Evidence will also be described which strongly suggests that the ingress of hydrogen may be related to the structure and properties of the oxide film(s) which are formed under given environmental circumstances.

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Introduction

The role of hydrogen in embrittlement of high strength Aluminum alloys, particularly those which are hardened by the $MgZn_2$ precipitate, has been a subject of controversy for some time. For monotonic loading cases the evidence of hydrogen embrittlement is still being debated, particularly since it is often difficult to unambiguously resolve the differences between what might be dissolution controlled stress corrosion cracking, and true hydrogen embrittlement. Under cyclic loading conditions however, many of the effects of environmental fracture may be accentuated and, assuming that a strong link can be forged between monotonic and cyclic loading, a considerable amount of information may be gained from an analysis of fatigue results in the Al alloys. The results discussed herein are a brief summary of a large number of experimental variables which have been examined to attempt to understand environmental degradation of the fatigue properties of high strength aluminum alloys. This environmental degradation is similar to that generally reported for monotonic loading, however there are several significant differences which are generally observed. Principally these differences include the fact that, for commercial alloys such as 7075 and 7050, in the peak hardened condition, fatigue cracks are transgranular. In some cases stage I cracking is observed, and in other cases only stage II cracking is observed. Also, because of the transgranular nature of cracking, coupled with sufficiently low crack growth rates when stage I cracking occurs, the crystallographic crack path has been identified as following either $\{100\}$ or $\{112\}$ planes in contrast to the $\{111\}$ crack propagation plane observed in dry air. These observations will be discussed in more detail in this presentation.

Experimental

The majority of the results discussed herein were obtained on a commercial extruded 7075 Al alloy, heat treated to the T6 condition and stressed in the longitudinal direction. In cases where it is relevant, the results of some experiments on a high purity Al5Zn2Mg alloy will be discussed. All experiments were performed on electropolished specimens under load control at 30 Hz. Environments included dry and moist air, aerated and deaerated 0.5 N NaCl, 0.5N Na_2SO_4 and 0.5 N H_2SO_4 . Anodic and cathodic polarization experiments were also performed. Additionally some specimens were pre-exposed to either NaCl or H_2SO_4 and subsequently tested for fatigue damage reversibility.

Results and Discussion

Sensitivity to Water Vapor

Under monotonic loading conditions moist air has been suspected to embrittle high purity Al alloys, although there is little evidence of such embrittlement in commercial alloys. Limited ductility of high purity ternary alloys which exhibit intergranular failure has been reported (1). The effect of water vapor is particularly important under cyclic deformation conditions, and as early as 1960, the decreased fatigue resistance of duralumin in moist air was associated with hydrogen evolved from the hydrolysis of water in growing cracks (2). Several workers have since shown that water vapor, in concentrations less than could produce capillary condensation in

Wei and co-workers, in particular, have demonstrated not only that water vapor is a damaging species but that surface reactions producing hydrogen may be the rate determining step for crack growth although the observed embrittlement is a bulk phenomenon (as contrasted to surface energy reduction due to adsorption of water vapor). There is no model for dissolution controlled stress corrosion cracking which can explain the results of water vapor on fatigue crack initiation or propagation.

Crack Path and Crystallography

Most studies of environmentally assisted crack propagation in high strength Al alloys have been performed in the crack propagation regime where stage II cracking dominates, and little can be said about the specific crystallographic morphology of crack propagation. Interestingly, however, some studies of very early crack propagation in water vapor in single crystals of AlZnMg alloys have shown that the surface topographies of stage I cracks are significantly different (6,7). Additionally these studies have shown that a shift in crack propagation path from stage I to stage II with decreasing frequency occurs only in water vapor. These results suggest that lower frequencies allow increased bulk diffusion to regions ahead of the crack tip where hydrogen presumably exerts its damaging effect. Under more severe conditions such as exposure to NaCl solutions or to other solutions under cathodic charging conditions, initial crack propagation in commercial alloys occurs in an essentially "featureless" zone which is approximately normal to the applied stress direction and appears to be non-crystallographic (Fig. 1). The extent of this region appears to be relatively independent of charging conditions and cracking appears to occur discontinuously after a considerable number of cycles (8). The featureless region is converted to a quasi-clearage region and finally to stage II crack propagation. In high purity analogues with equiaxed grain structures only the quasi-clearage region is observed, although at low applied stresses



Fig. 1. "Featureless" early crack propagation zone associated with environmental fatigue of 7075-T6 Al, initiated at an inclusion. Similar zones can be identified for free corrosion or cathodic charging conditions in virtually all electrolytic solutions.

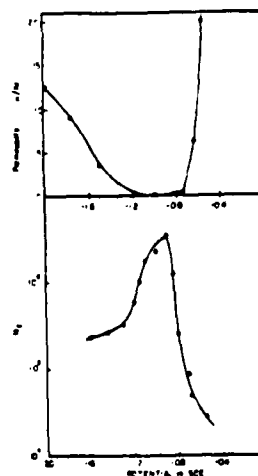


Fig. 2. Correlation of hydrogen permeability experiments (11) with fatigue life in 0.5 N NaCl as a function of applied potentials. $\phi_{\text{corr}} \approx -0.7V$ vs SCC.

transgranular propagation (9). The results of these experiments cannot be associated with a dissolution process unless it is assumed that dissolution is the rate determining step for hydrogen evolution. Rather these observations are consistent with a mechanism where a dissolved solute in the metal (presumably hydrogen) reaches a critical concentration leading to cracking, and is only indirectly associated with deformation. For example, at moderate to high stress levels, or when stress concentrations are sufficiently large, extensive slip is believed to result in dislocation transport of hydrogen into the lattice, while at lower stresses the preferred transport path is along grain boundaries. This latter hypothesis may in fact be the link between "SCC" and "corrosion fatigue" of these alloys since cyclic deformation could be expected to be a much more effective transport mechanism of hydrogen into the lattice for sufficiently high stresses or hydrogen fugacity. It may also be significant that the reported fracture path in single crystals of these alloys appears to be either along {112} or {100} planes. These planes have been reported to be the interfacial planes between the $MgZn_2$ precipitates and the matrix and there is a temptation to consider that these interfaces would be potential sinks for hydrogen. This process would be analogous to that reported by Swann and co-workers for monotonic loading, where the grain boundaries become the preferred enhanced diffusion path and separation is observed along non-coherent precipitate matrix interfaces, with no apparent corrosion attack of either phase at electron optical resolutions.

Hydrogen Damage Reversibility

Precharging of 7075 T6 Al with hydrogen by cathodic charging in either 0.5 N NaCl or in 0.5 N H_2SO_4 results in a significant reduction in fatigue resistance. In the former case significant corrosion occurs at non-metallic inclusions while for the latter case, little or no corrosion of the alloy occurs. For both cases, however, post charging heat treatments, consisting of resolutionizing of the alloy at $460^\circ C$ followed by re-aging at $120^\circ C$, results in significant recovery of fatigue properties. Increasing the resolutionizing time at temperature results in still larger degrees of fatigue resistance recovery, although for the NaCl case the damage associated with the inclusions precludes total recovery (Table I).

Table I. The Effect of Re-Heat Treatment Duration on Subsequent Fatigue Properties in Air

Pre-Corrosion: 24 hours in aerated 0.5 NaCl	
Re-heat treat: Solutionize at $470^\circ C$ for x hours	
Age at $121^\circ C$ for 24 hours	
Fatigue in air: Mean stress 276 MPa, Cyclic Stress \pm 96 MPa	
<u>Time at $470^\circ C$</u>	N_f
0 hours	30,000 cycles
3 hours	85,000 cycles
6 hours	101,000 cycles
24 hours	> 13,000,000 cycles*

*Equivalent to tests in dry air without pre-exposure.

It is important to note that control specimens, fatigued in dry laboratory air after similar "baking" experiments show no effect of cyclic heat treatments. Thus, it may be concluded that the hydrogen effect in these alloys is essentially reversible, presumably by removing dissolved hydrogen from the alloy lattice. No classical mechanism of stress corrosion cracking, or of corrosion assisted fatigue can explain these results.

Electrochemical Parameters

It has been shown that environmentally affected fatigue of these alloys, under cathodic charging conditions is virtually independent of the type of anion, eg. Cl^- or SO_4^{2-} or of the anionic strength of the solution eg. pH 0.6 to 10 (10). Additionally it has been shown that a maximum in fatigue resistance is observed at a potential which is virtually identical with that where hydrogen permeation has been shown to be a minimum in these alloys (Fig. 2). Thus, the presence of hydrogen is sufficient to cause significant decreases in fatigue resistance independent of chemical attack of the protective passive films. It cannot be concluded however, that chemical attack of passive films is not important to fatigue resistance, *per se*, since it has also been shown that, in the absence of externally produced hydrogen (charging), chloride ion is certainly more damaging than sulfate ion (Fig. 3a), which is in turn more damaging than de-ionized water. However, acidic

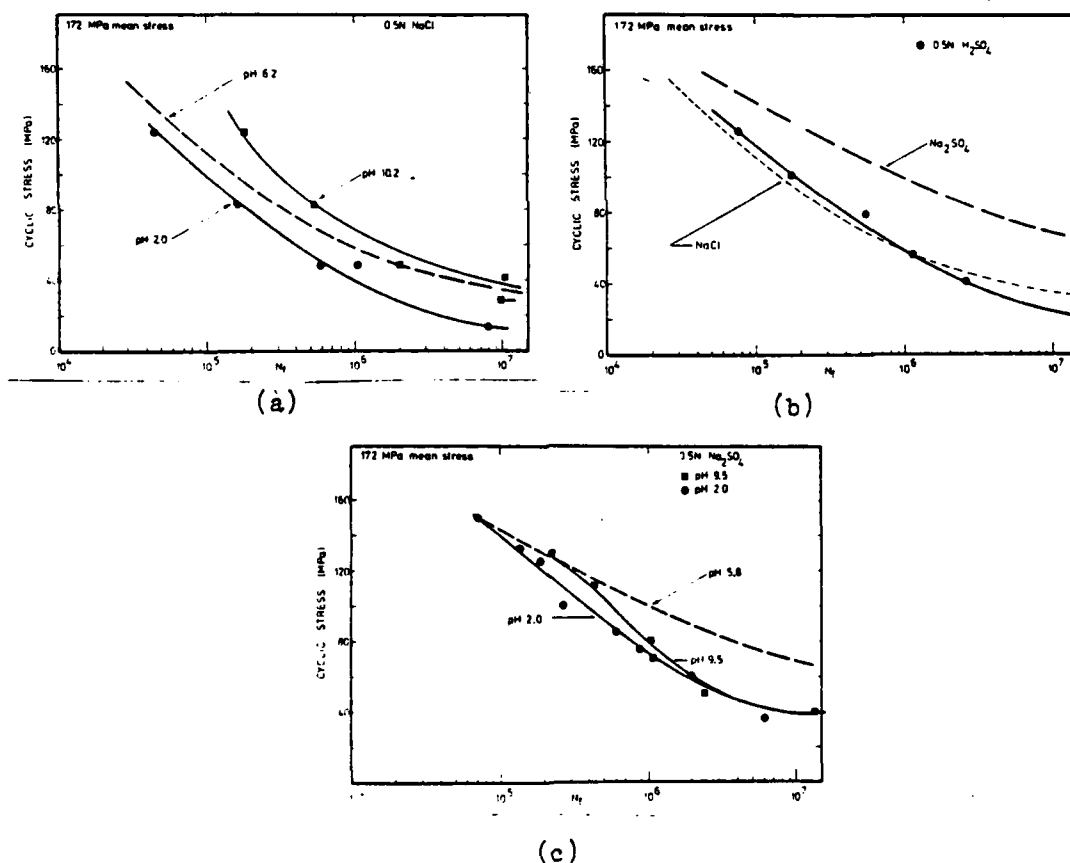


Fig. 3. The effects of anion species and pH on the fatigue resistance of 7075 Al alloy. a) effect of pH in NaCl solution, b) comparative effects of neutral Na_2SO_4 , neutral NaCl and 0.5 N H_2SO_4 (pH 0.6) c) effects of pH in Na_2SO_4 solutions. In general, corrosion rates are least at neutral pH and are equal for pH 2 and ~pH 10 in Cl^- and SO_4^{2-} solutions.

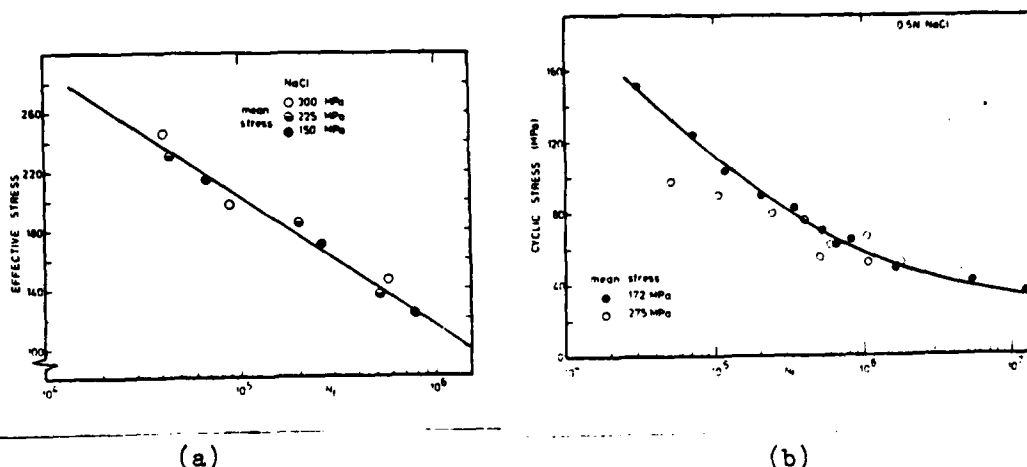


Fig. 4. a) Correlation of effective stress, normalized for different mean stress on fatigue resistance of 7075 Al alloy in 0.5 N NaCl solution b) Fatigue resistance of 7075 Al in 0.5 N NaCl solution as $f(\sigma_{\text{cyclic}})$ for two mean stresses. The divergence at high cyclic stresses can be eliminated by correlation with "effective" stress range (12).

solutions are not necessarily more damaging than neutral solutions, under free corrosion conditions (Fig. 3b). Neutral Sulfate solutions of pH 2 and pH 9.5 at low stresses are an exception in that both environments lead to equivalent decreases in fatigue resistance (Fig. 3c).

Mechanical Parameters

Normalization of mean stress effects on environmental fatigue of 7075 Al in distilled water, NaCl and Na_2SO_4 solutions under freely corroding conditions, and under cathodic charging conditions, indicate that neither mean stress or maximum stress in a given cycle control fatigue damage (Fig. 4a). Rather, these results indicate that the cyclic stress range is the critical mechanical parameter which controls fatigue resistance (Fig. 4b).

Additionally, experiments performed under nominal Mode III (torsional) cyclic loading indicate that there is little effect of corrosion or of cathodic charging on fatigue resistance for this loading condition (Fig. 5). These results are to be expected if it is assumed that significant hydrogen transport or accumulation in the alloy necessitates a hydrostatic stress component in the vicinity of the alloy surface or near a crack tip. However, if metal dissolution is the critical process in environmental fatigue, no appreciable difference in Mode I vs Mode III loading should be expected (neglecting transport in the liquid inside the crack).

A Model for Hydrogen Assisted "Corrosion Fatigue" of Al Alloys

The results of these and other investigations strongly suggest that dissolved hydrogen in the alloy lattice is a critical species in determining the fatigue resistance of high strength aluminum alloys. Under corrosion conditions hydrogen may be effectively blocked from entry to the alloy by

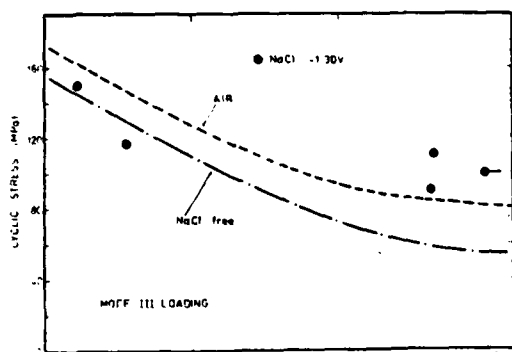


Fig. 5. Effect of Mode III loading in fatigue resistance of Al alloy in air, NaCl solution under free corrosion and hydrogen charged in NaCl solution showing little or no effect of environment.

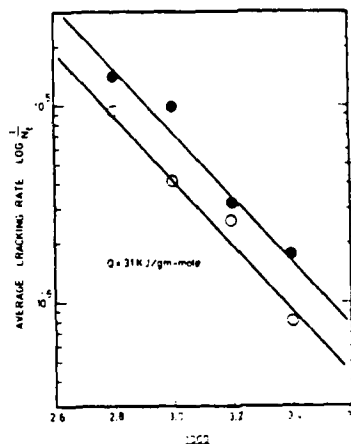


Fig. 6. Activation energies for apparent crack propagation in Al alloys pre-exposed in 0.5 N H_2SO_4 for one hour (open circles) and for 24 hours (closed circles) and subsequently fatigued in distilled water.

the presence of the adherent passive film which is naturally formed on the alloy. Exposure to NaCl, or to solutions of high or low pH effectively damages this film allowing ready access of bare metal for hydrogen entry. Thus fatigue lives are improved in less aggressive solutions such as distilled water or neutral Na_2SO_4 . In these cases hydrogen entry is apparently blocked during the initiation and early crack growth stages, however as the crack propagates, hydrogen entry is facilitated by mobile dislocations in the vicinity of the crack tip. It is significant to note that experiments conducted either by pre-exposure to H_2SO_4 solutions for 4 hours and for 16 hours followed by fatigue in distilled water as a function of temperature show essentially the same apparent activation energy for average crack propagation rate ($1/N_f$) (Fig. 6). The apparent cracking rate is $\sim 2x$ indicating a strong correlation with a diffusion process obeying a parabolic relation with diffusional distance.

To summarize, it appears that the rate determining process in environmental fatigue of high strength Al alloys is the absorption of hydrogen into either the alloy surface or into the plastic zone ahead of a growing crack. Hydrogen ingress during initiation may be facilitated by chemical means such as Cl⁻ environment, high or low pH, cathodic charging, etc., or by mechanical means such as slip band rupture of protective films. During the early propagation stages hydrogen ingress is further facilitated by crack tip chemistry and the large amounts of deformation associated with crack tip stress and strain concentrations. In every case, it is believed that a critical rate determining step is important to the process and that the rate determining step may be different for different environmental conditions. Some of the steps which might be involved could be hydrogen dissociation, absorption diffusion, concentration etc. and these steps may be further determined by hydrogen fugacity, chemical or mechanical rupture of oxide films, or even a sufficient local corrosion rate to support sufficient amounts of hydrogen generation and absorption. However, while the rate determining step may differ for different chemico-mechanical conditions, the fact remains that the evidence presented here strongly supports a hydrogen embrittlement phenomenon as the cause of environmental fatigue of these high strength Al

alloys. The vexing problem remains, however, that while dissolved hydrogen is an embrittling agent, there is still no direct evidence for the specific mechanism(s) associated with this phenomenon.

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